INVESTIGATOR'S ANNUAL REPORT

United States Department of the Interior

National Park Service

All or some of the information you provide may become available to the public.

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Reporting Year:	**Park:**	**Select the type of permit this report addresses:**
2008	Shenandoah NP	Scientific Study

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Project Title (maximum 300 characters):

Linked Hydrologic and Atmospheric Mercury Fluxes in a High-Elevation Wetland

Park-assigned Study or Activity #:	**Park-assigned Permit #:**	**Permit Start Date:**	**Permit Expiration Date:**
SHEN-00340	SHEN-2007-SCI-0010	Jun 20, 2007	Mar 31, 2012

Scientific Study Starting Date:	**Estimated Scientific Study Ending Date:**
Jun 20, 2007	Mar 31, 2012

For either a Scientific Study or a Science Education Activity, the status is:

Continuing

For a Scientific Study that is completed, please check each of the following that applies:

__ A final report has been provided to the park or will be provided to the park within the next two years

__ Copies of field notes, data files, photos, or other study records, as agreed, have been provided to the park

__ All collected and retained specimens have been cataloged into the NPS catalog system and NPS has processed loan agreements as needed

Activity Type:

Research

Subject/Discipline:

Wetlands / Floodplains

Purpose of Scientific Study or Science Education Activity during the reporting year (maximum 4000 characters):

The accumulation of mercury (Hg) in the environment from atmospheric deposition is a worldwide problem that has gained attention relatively recently [Krabbenhoft, 2004]. The form of mercury that is particularly toxic is methylmercury (MeHg), which is formed by

the bacterial transformation of ionic mercury (Hg2+) and efficiently bioaccumulates in the food chain. It is estimated that approximately 630,000 children born each year in the U.S. alone are exposed to elevated methylmercury levels in the womb, putting them at risk of impaired neurological development [Mahaffey, 2004]. Only now are we beginning to fully grasp the widespread impact that this problem is having on human health, affecting localities hundreds of miles away from emission sources [Driscoll et al., in press]. Mercury concentrations in the atmosphere have increased 2-5 times those of pre-industrial levels [EPA, 1997] leading to increased deposition. However, it is the transformation processes that occur upon deposition within watersheds that ultimately affect the bioavailability of this toxin. Although the impact of the mercury problem is wide-ranging, the specific processes that control mercury cycling in the environment remain poorly understood.

Statistical relationships between watershed physical descriptors and mercury concentrations are relatively weak, but two key controls are worth noting. First, the degree of watershed forestation is positively related to Hg concentration since trees scavenge Hg vapor through stomatal uptake [Ericksen et al., 2003] and because organic matter is typically abundant in forested systems. Second, watersheds with wetlands tend to have high concentrations of MeHg, since reducing conditions are more favorable in these areas [Grigal, 2002]. Overall, controls on mercury concentrations are quite complex, and high spatial variability can be found within limited geographical areas. For example, preliminary measurements taken in Shenandoah National Park (SNP), Virginia at 15 sites found HgT concentrations to be fairly low, ranging from 0.104 ng/L to 0.651 ng/L. Deviations from these low levels were discovered in the Big Meadows area of SNP, an extensive wetland area that is the location of the proposed research. Here, total mercury concentrations in surface water were much higher, ranging from 1.77 ng/L to 4.66 ng/L [C. Moore., pers. comm.]. These concentrations are consistent with a setting in which bioaccumulation of mercury is a general problem. Streams that drain this wetland area, however, have reduced total mercury concentrations, raising the question of which transformations and fluxes are responsible for dramatically altering the stream mercury concentrations along the hydrological flowpaths within the wetland.

We would like to develop a processed-based understanding of how mercury is transformed in natural environments by simultaneously measuring both aqueous and atmospheric fluxes. The large gradient in mercury levels over short distances in the Big Meadows area of SNP provides us with an ideal natural laboratory to understand how mercury moves through the natural environment. The ultimate goal is to scale up this information to predict other areas within SNP that are vulnerable to elevated stream water levels of mercury and mercury bioaccumulation.

Findings and status of Scientific Study or accomplishments of Science Education Activity during the reporting year (maximum 4000 characters):

For our research in Shenandoah National Park, we have completed two of our planned four week-long campaigns measuring total gaseous mercury fluxes in the Big Meadows area. We used a modified Bowen Ratio technique to measure these fluxes, which included the deployment of eddy covariance equipment on a portable tower. These successful measurement campaigns, will serve as the basis for graduate student Amber Converseâ s M.S. thesis, were augmented by dew collection in an effort to quantify the amount of mercury that reaches the land surface through dew deposition. Amber defended her M.S. proposal in June, 2008 and is on track to graduate in summer 2009.

Ph.D. student Ami Riscass has focused on mercury in stream water within Shenandoah National Park. She has worked closely with undergraduate student Kelly Hokanson to develop an automated technique to collect stream water samples for mercury analysis. They have done this by retrofitting ISCO automated samplers with Teflon parts and have conducted a series of tests to quantify any errors that might be associated with line contamination, bottle contamination, and the possibility of mercury evasion from water samples that have been collected. Ami recently presented the results of this study at the 2008 American Geophysical Union (AGU) Fall meeting, and is currently preparing this for publication. They have also deployed modified ISCOs at three catchments where discharge and stream chemistry measurements are collected as part of the Shenandoah Watershed Study program. This site setup will enable us to measure time series of total mercury concentrations over the course of storm events, which is critical to understanding mercury dynamics in catchments. The goal is to understand how mercury is mobilized and associated with sediment and various forms of organics.

Atmospheric mercury fluxes collected in Shenandoah National Park showed major differences between the summer and fall measurement campaigns. During the summer there was distinct diurnal variability, while fall data lacked this feature. Although many previous studies have pointed to stomatal processes as dominating land-atmosphere exchange of mercury, our data showed no significant correlation between mercury fluxes and stomatal conductance. Mercury fluxes were significantly correlated with the intensity of ultraviolet radiation during the summer, but no such significant correlation existed in the fall. Upcoming measurement campaigns will take place during the winter and spring. The objective is to determine the dominant controls on mercury deposition and emissions, and how these controls vary on a seasonal basis.

Tests of ISCO automated samplers retrofitted with Telflon tubing has shown that only minor differences exist between mercury concentrations in water collected by this method versus water collected by more traditional grab sampling. Evasion of mercury from collected appears to be the main contributor to potential errors, but cumulative errors were still found to be within the acceptable limits recommended by the EPA.

For Scientific Studies (not Science Education Activities), were any specimens collected and removed from the park but not destroyed during analysis?

No

Funding specifically used in this park this reporting year that was provided by NPS (enter dollar amount):	**Funding specifically used in this park this reporting year that was provided by all other sources (enter dollar amount):**
$0	$35000

List any other U.S. Government Agencies supporting this study or activity and the funding each provided this reporting year: